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FINAL REPORT ON

CHARACTERISATION OF SOLID ELECTROLYTES

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MICROMEDIA

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Summary

Samples of polycrystalline NYS and NGS were very sensitive to electron beam damage. Preliminary investigations showed the presence of dispersed particles of a glassy-type phase. The Edax analysis shows this glassy phase has a markedly higher concentration of Si compared to the matrix in both NYS and NGS.

Des echantillons de NYS et NGS polycristallins s'avéreut trés sensibles a rayon d'electrons. Ces premieres examens ont monteé la presence de particles de type vitreuses dispersee dans la matrice. Ces analysis "EDAX" prouvent que cette phase vîtreuse correspond à une haute concentration en Si compareè a celle des matrice de NYS et NGS.

I. INTRODUCTION

Sintered pellets of 6N3, NYS and NGS were prepared for ion exchanging to their hydrogen-conducting forms. The compositions and preparation techniques are described and the results of microstructural analysis are discussed.

II. SAMPLE PREPARATION

The optimum composition with respect to density and f(β) contains 60 wt% total alkali as Na_2O, 40 wt% as K_2O, 3 wt% MgO and the balance Al_2O_3. The optimum sintering temperature was 1610°C for 3-5 minutes.

A two stage ion exchange procedure was identified as optimum. The Na^+ was first exchanged wholly or in part by K^+ from molten salt chlorides or nitrate melts of controlled Na^+ and K^+ activity. The K-exchanged electrolytes were immersed in concentrated H_2SO_4 at 350°C or exchanged with field assistance at ~ 100°C.

Mixed water-based solutions of 0.1 M, 0.2 M and 0.3 M with respect to rare-earth atoms (Gd or Y) were prepared from gadolinium acetate (99.9% pure) for NGS or yttrium nitrate (99.9% pure) for NYS, sodium carbonate (reagent grade) and sodium silicate (Na_2O/SiO_2 = 1/2 w/w). Solutions were spray-dried in a spray drier and solutions were atomized from the top.

Calcined powders were isostatically pressed at 30 to 60 Kpsi into pellets and bars and sintered at 1000 to 1100°C (NGS) and 1100 to 1200°C (NYS) for less than 30 minutes.

NKGS was obtained by conversion of NGS in NaCl/KCl melts at 800°C. To avoid cracking, the ion exchange was done by immersion in consecutive melts of low to high $[K^+]$ (= ca. 0.5). HNGS was prepared from both NGS and NKGS in 0.1 M CH_3COOH by FAIE at 25° to 90°C.

III. MICROSTRUCTURAL EXAMINATION OF 6N3

Sample preparation for electron microscopic examination is a very important factor in E.M. characterization of materials. A lapping machine capable of thinning a pellet to 30 to 50 μm in kerosene was set up. Final thinning was achieved by ion bombardment.

A Commonwealth Scientific Corporation IMMI II machine required major repairs and was fixed up for ion thinning the lapped samples. Ion thinned samples of 6N3 were found to be highly susceptible to electron beam damage. In order to make the samples more stable under the electron beam the highly mobile Na and K atoms in 6N3 were ion exchanged for less mobile divalent cations such as Ca and Sr. The choice of these cations was also guided by the fact that they preferentially exchange in β''-Al_2O_3 compared to β-Al_2O_3. Thus such cations could also serve as tracers to distinguish between the β-Al_2O_3 and β''-Al_2O_3 grains.

III.1 Divalent Cation Exchange

A salt mixture of $CaCl_2$ and NaCl in 6:4 molar ratio was used at 770°C. Ion exchange was monitored by (1) x-ray diffraction, (ii) x-ray fluorescence, and (iii) EDAX analysis in the STEM.

Figure 1 shows x-ray diffractometer traces of a 6N3 pellet before and after Ca exchange. The (110) and (220) peaks show no change of position indicating that the a-parameter remains unaltered during Ca exchange. Other peaks with $\ell \neq 0$ shift towards higher θ values indicating a shortening of the Co-parameters in both β- and β''-Al_2O_3 exchange. This agrees with other workers results. X-ray fluorescence and EDAX analysis confirmed the Ca exchange in 6N3 pellet.

Similar observations were also made in the Sr exchange experiments. A 6:4 molar ratio of $SrCl_2$ and NaCl salt mixture at 700°C was used and the exchange was fairly fast. The Sr-exchanged samples were found to be superior vis a vis stability in the electron beam.

III.2 Electron Microscopy

The electron microscopic examination of 6N3 pellets showed that it is a very fine grained material of submicron size. The grains are lamellar with widths ~ 0.1 μm. Therefore a VG MB5 scanning transmission electron microscope was used for examination because of its high spatial and microanalytical capability. The general microstructure consists of individual grains of pure β- and β''-Al_2O_3 and intergrowths of β- and β''-Al_2O_3 grains. One has to use convergent beam microdiffraction which results in superposition of diffraction discs. Therefore usual orientations for this purpose in the hexagonal and trigonal systems are not useful and high index reciprocal lattice planes must be used for identification purposes. This is usually tedious and often involves ambiguity. Therefore divalent cations were exchanged in place of the mobile Na^+ and K^+ to act as tracers via their differential rate of exchange with the β- and β''-alumina phases.

Figure 2 shows the general microstructure of polycrystalline the 6N3 material and Figures 3 and 4 are microdiffraction patterns of individual grains of β- and β''-Al_2O_3 respectively. Figure 5 shows a lattice image of a grain showing intergrowth of β- and β''-Al_2O_3 phases. No grain boundary phase has been detected in any sample analysed.

III.3 X-ray Microanalysis

EDX analysis in the STEM encounters difficulties in assessing the $[Na^+]$ and $[K^+]$ because of their high mobility under electron beam irradiation. This is particularly true when analysing the Na/K content of individual grains of submicron size (~ 0.1 μm) as this requires smaller probe sizes and therefore a higher dose of electrons per unit volume. Monitoring the x-ray count ratio of Al to K in the spot scan mode for different grains showed that the potassium concentration in different grains varies over a wide range.

The ratio of Al to mobile atom x-ray counts is considered a more reliable index for monitoring the mobile ion concentration because it reduces the ambiguity in events due to thickness and orientation differences between different grains.

After ion exchange with divalent cations like Ca^{2+} and Sr^{2+} it was observed that the sample became relatively more stable in electron irradiation. A notable feature of the ion exchange by divalent cations was that the $[K^+]$ is totally replaced even when the sample is only partially exchanged. A typical Al^{3+}/Ca^{2+} x-ray count ratio in an exchanged sample is as follows.

General Area Scan	Spot Scan	
	β''	β
4.4 ± .3	8 ± 3	17 ± 3

This shows that the overall Ca^{2+} concentration detected in the sample is markedly higher than the spot scan over individual β- and β''-Al_2O_3 grains because of the migration of Ca^{2+} in the small focussed probe of the spot scan mode. Even so a marked difference in Ca^{2+} concentration in β- and β''-Al_2O_3 grains was observed and is good enough to distinguish the individual grains. Therefore, even though the quantitative estimation of Ca^{2+} or Sr^{2+} in β- and β''- Al_2O_3 grains is not possible, their relative values clearly identifies the two types of grains and suggests the original K^+ was concentrated in the β-Al_2O_3 phase.

A detailed examination of grain boundaries and grain boundary phases is in progress.

IV. MICROSTRUCTURAL EXAMINATION OF NYS AND NGS

Samples of polycrystalline NYS and NGS were very sensitive to electron beam damage. Preliminary investigations showed the presence of dispersed particles of a glassy-type phase. The EDAX analysis shows that this glassy phase has a markedly higher concentration of Si compared to the matrix in both NYS and NGS.

Figures 6 and 7 show the general microstructure of NYS and NGS respectively. Figure 8 shows a typical electron diffraction pattern from a NYS grains. The glassy phase was not always observed and when it was, it was in isolated pockets in the microstructure (Figure 9).

Figure Captions

Fig. 1 X-ray diffractometer trace showing shifts in the peaks indicating contraction of c-parameter after ca exchange.

Fig. 2 General microstructure of a Sr exchanged 6N3 pellet indicating submicron grains. No grain boundary phase is observed.

Fig. 3 Microdiffraction of a β grain.

Fig. 4 Microdiffraction of a β'' grain.

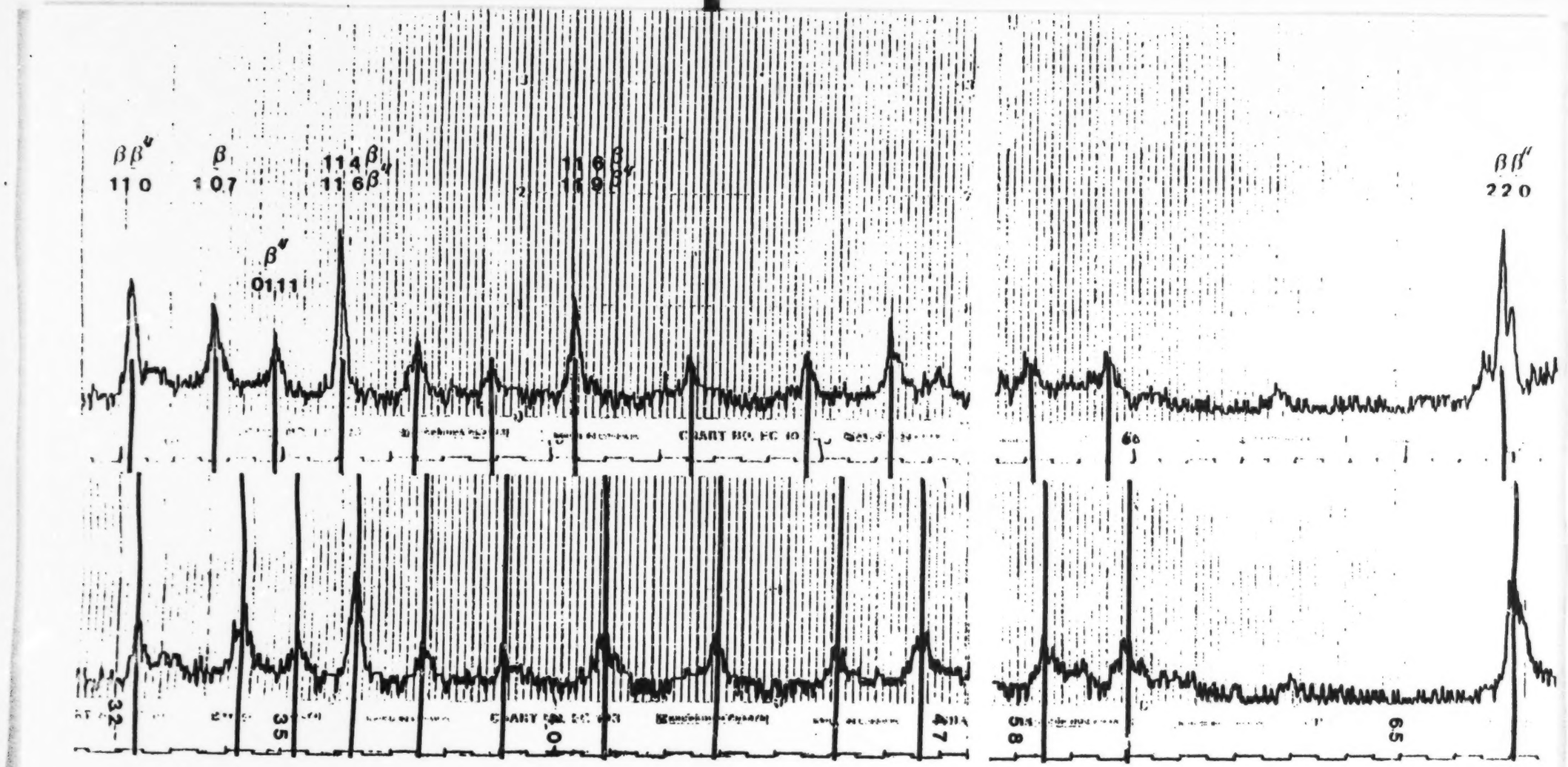
Fig. 5 Lattice image of a grain showing intergrowth of β and β''.

Fig. 6 Microstructure of NYS pellet.

Fig. 7 Microstructure of NGS pellet.

Fig. 8 Selected arc diffraction pattern of NYS.

Fig. 9 Micrograph of glassy-phase pockets in NYS.



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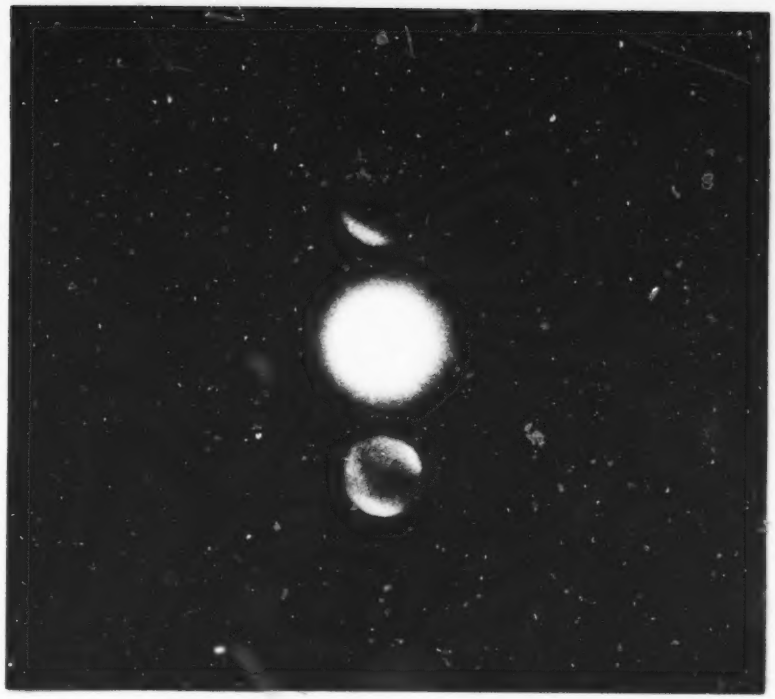

Fig. 3 Microdiffraction of a B grain

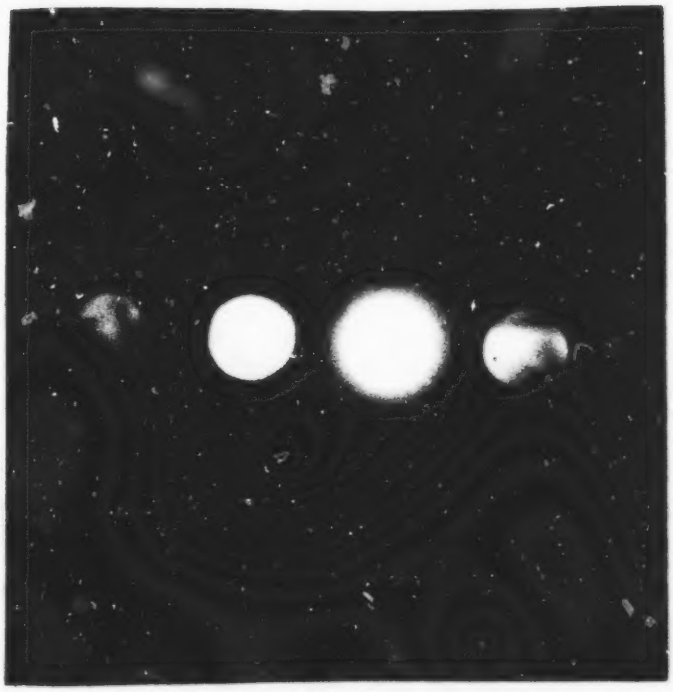

Fig. 4 Microdiffraction of a B" grain

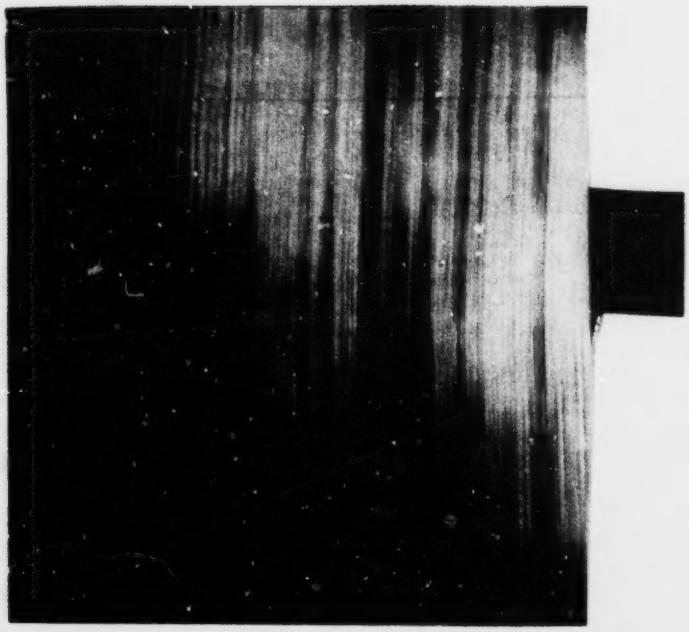

Fig. 5 Lattice image of a grain showing intergrowth of B and B".

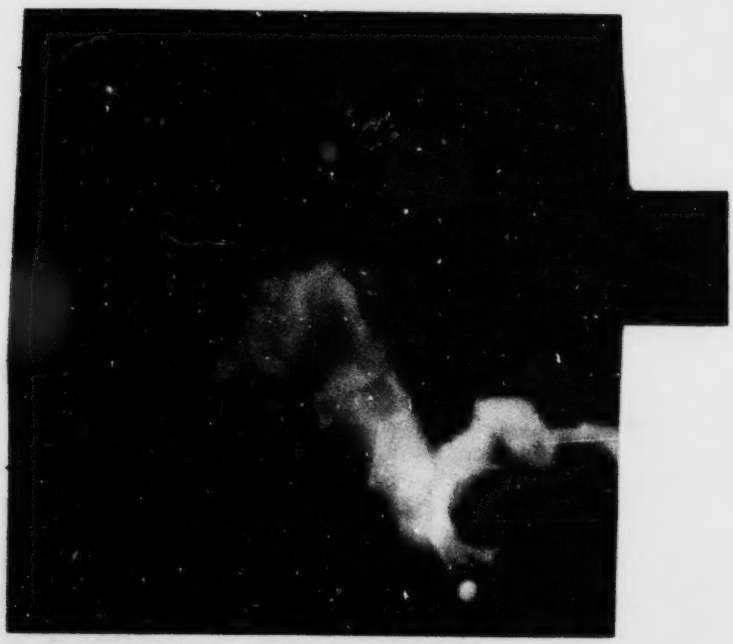

Fig. 6 Microstructure of NYS pellet

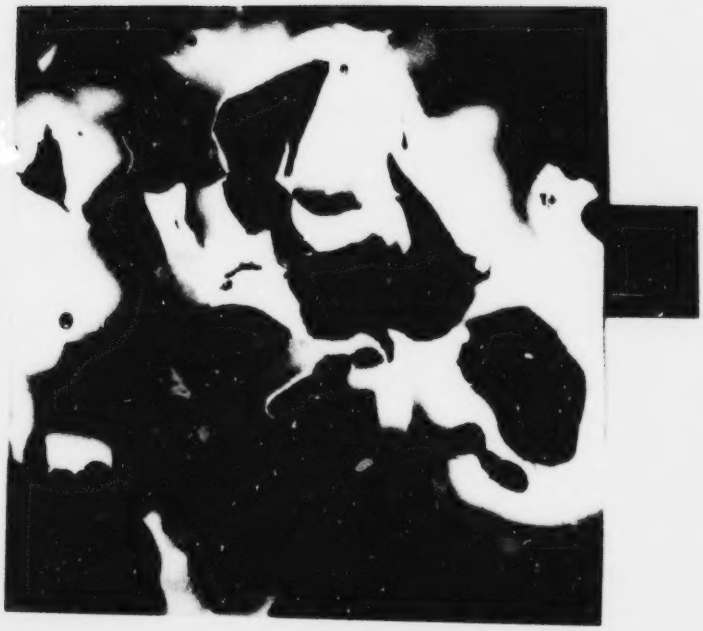

Fig. 7 Microstructure of NGS pellet

Fig. 8 Selected area diffraction pattern of NYS

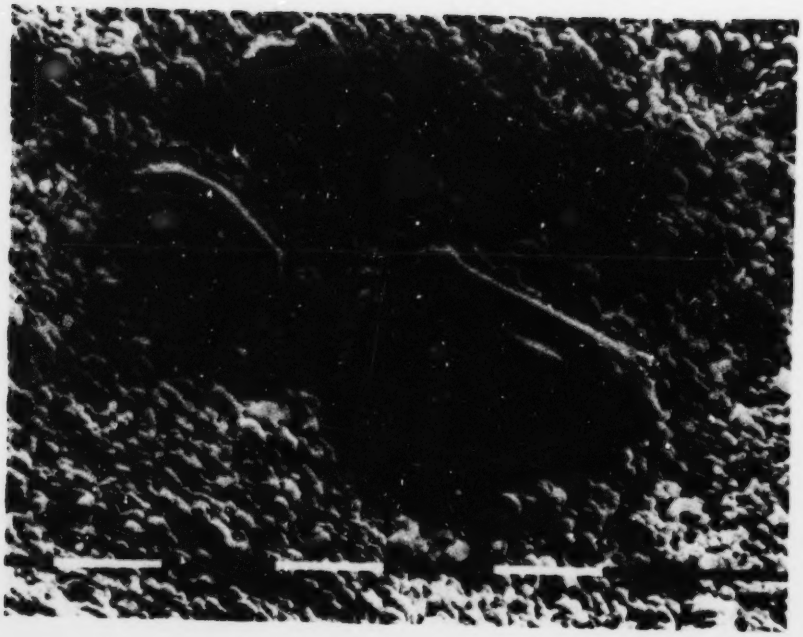

Fig. 9 Micrograph of glassy-phase pockets in NYS.
One marker = 100 μm